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Ion Assisted Deposition of Fiber Coatings for Ceramic Matrix Composites with Low Dielectric Loss Tangents

Overview

The research for this project has yielded significant progress in the past year. The preliminary goal of achieving facility in the growth and characterization of thin amorphous silver nitride films was reached without difficulty. Thermal annealing studies resulted in the discovery of both bubble formation and crystallization in the film. These novel phenomenon were investigated further.

As anticipated in the project proposal this research can naturally be divided into three segments. First is the fabrication of the amorphous films themselves. Second, the thermal stability of the films on various substrates would be investigated. Thirdly, the knowledge obtained about the structure and properties of the material would be utilized in understanding and further refining the science of thin film deposition. These divisions were reflected finally in the preparation of three publications, which together comprise a complete record of the progress made this past year. The three

papers are included here.

The first paper is entitled Near Infrared Rugate Filter Fabrication by Ion Beam Assisted Deposition of $Si_{(1-x)}N_x$ Films. It has been submitted for publication to the journal Applied Optics. The major emphasis of this paper is on the optical properties of the films. It nevertheless includes an excellent description of the work done to fabricate silicon nitrite films. The experimental system is presented and the procedure used to predict the film composition from the experimental parameters is outlined. Certain features of the film's physical and mechanical properties are discussed.

The second paper was submitted for publication in the journal Nuclear Instruments and Methods B and is entitled Thermal Stability of Silicon Nitride Coatings Produced by Ion Assisted Deposition. The properties of the film both as deposited and after annealing are discussed. Rutherford backscattering, infrared spectroscopy, electron microscopy and X-ray diffraction were used to characterize the samples. While none of the films seemed to have diffused into the substrate after annealing, blistering and crystallization did occur in certain samples indicating inherent limitations of this material for fiber coating applications.

The morphology of silicon nitride crystallization in the film was investigated further. The occurrence of both spherulitic and fractal aggregates in the crystallized films was discovered. This fact showed the amorphous film system to be very interesting from a crystallographic viewpoint. The growth

and morphology of the crystal aggregate was indicative of the interplay between atomic diffusion, impurity concentration and competing mechanisms for crystallization. As a result of these studies it seems possible that film stability at high temperatures could be produced if impurities such as copper were eliminated and the stoichiometry of the films was more carefully controlled. THese studies are presented in the paper Fractal and Spherulitic Morphology of Silicon Nitride Crystallized from Amorphous Films, which was submitted for publication to Physical Review Letters.

Near Infrared Rugate Filter Fabrication by Ion Beam Assisted Deposition of $Si_{(1-x)}N_x$ Films

E.P. Donovan, D. Van Vechten, A.D.F. Kahn, C.A. Carosella, and G.K. Hubler

ABSTRACT

The near infrared refractive index of amorphous silicon nitrogen alloy films decreases continuously as the composition varies from pure silicon to stoichiometric silicon nitride (Si_3N_4). Homogeneous and inhomogeneous films up to five micrometers in thickness have been produced by simultaneous deposition of ion beam nitrogen and electron beam evaporated silicon. Film properties include environmental stability, resistance to chemical attack, high hardness, thermal stability and adherence to the substrate. Film index of refraction depends upon the relative fluxes of beam and evaporant. Band rejection filters of the rugate design were fabricated in which the index was sinusoidally varied with depth.

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Introduction

The term "Rugate" is descriptive both of the corrugated, sine-wave, refractive index depth profile of the single rejection band filter and of the desired film ruggedness against environmental stresses. The design can be understood as a variation of the quarter wave dielectric stack. There, layers of pairs composed of 1) high index (n_H) material of thickness $\lambda/4n_H$, and 2) low index (n_L) material of thickness $\lambda/4n_L$ are sequentially deposited on a substrate of index n_S. For light of wavelength λ at normal incidence, the reflectivity in air for M such layer pairs with no absorption is [1]

$$R = (1-n_S(n_L/n_H)^{2M})/(1+n_S(n_L/n_H)^{2M})^2 \approx 1-4n_S(n_L/n_H)^{2M} \qquad (1)$$

where the approximation is true for small $(n_L/n_H)^{2M}$. High reflectivity with few layer pairs requires a large difference in index, and implies quite different compositions, crystal structures, and thermal expansions between the two layer materials. Interlamellar delamination is a problem under thermal cycling for the quarter wave stack whose layer pairs differ in thermal expansion.

The simple rugate filter [2] consists of layers whose indices of refraction follow a sine wave cycle. The index oscillates around the average index n_o with an amplitude $\Delta n/2$ with period $2l/4n_o=l/2n_o$. In model calculations the reflectivity at λ increases as the number of cycle layers increases at a given Δn, and for larger Δn at a set number of cycles [3]. The index profile for a multi-line rejection filter is obtained by summation of the sinusoid for each line since the principle of superposition applies. A rugate filter material which retains its structure through the range of Δn

should greatly reduce the probability for interlamellar delamination and be more rugged than the quarter wave stack.

The fabrication method for filters must produce environmentally stable films. Conventional vacuum deposition techniques produce films subject to several faults. These include high internal stress, poor adhesion to the substrate, and high porosity which causes irreversible and unpredictable index changes when exposed to humid air. In many materials, a beam of energetic particles incident upon a film during deposition improves optical, structural, mechanical and other properties of the film [4]. For example, internal stress was relieved in germanium films evaporated with an Argon ion beam assist, provided that an energy dependent minimum arrival rate ratio of ions to evaporant atoms was exceeded [5]. Computer simulation showed that the energy dependence could be understood in terms of the spatial (not temporal) overlap of the collision cascades generated as the ions come to rest [6]. Film stress relief thus occurs when each film atom has at least one opportunity to change position. Generalization of this analysis to the nitrogen IBAD of silicon process indicated that the critical arrival ratio to produce low-stress films is far exceeded during rugate production. Thus rugate filters fabricated by IBAD should be superior to filters fabricated by evaporation.

In this paper we attempt to demonstrate that nitrogen ion beam assisted deposition of amorphous silicon nitrogen alloy films is a useful technique for the production of rugged near infrared rugate filters.

Experimental

Typical base pressure of the cryopumped bell-jar deposition chamber

(Figure 1) is $4x10^{-5}$ Pa without baking. Pressure is maintained at 0.0266 Pa during operation of the ion source. An alignment system ensures that the ion beam can be centered on the sample mount using three Faraday cups arranged in an equilateral triangle around the sample. The Faraday cup design incorporates an aperture biased by negative 100 volts to repel stray electrons and prevent the escape of secondary electrons produced when the ions strike the cup interior. Samples may be water cooled. Ion-source-to-sample distance is 27 cm, and the beam has normal incidence to the substrate. Evaporator-to-sample distance is 30 cm, 20^{o} off sample normal. A quartz crystal oscillator shielded from the beam is used for evaporant rate control (usually 0.5-1.0 $^{nm}/_{sec}$ silicon deposition rate). A personal computer monitors the evaporation controller and the current integrator, and controls the ion source-beam voltage (500 eV) and extracted current (3-40 mA) during deposition. Pure silicon substrates cut from silicon wafers were sputter cleaned with nitrogen prior to deposition. The dose for sputtering was sufficient to make the near surface layer amorphous, which should remove substrate orientation effects. The usual practice was to mount a back-roughened substrate for reflection measurements next to a doubly polished one for transmission measurements. Some homogeneous films were deposited on graphite, glass, quartz and alumina substrates with good substrate adhesion.

Homogeneous film compositions were measured by Rutherford backscattering spectroscopy (RBS) [7] and analyzed using the Cornell University program [8]. Reflection and transmission spectra were measured on the Perkin-Elmer Lambda9 Spectrometer. Refractive indices were determined from fits to the reflection interference spectra based on multi-layer calculation methods described in

the text by Heavens [9]. Index values quoted in this paper are those at 6000 cm-1 in wave number. The rugate filters were typically annealed at 750 C in an argon atmosphere to reduce absorption.

Rugate Fabrication by Ion Implantation

Ion implantation of nitrogen into crystalline silicon substrates, held at elevated temperatures to remain crystalline, was found to change the refractive index of the implanted layer [10]. The index profiles were determined from fits to infrared reflection spectra and were correlated with the composition profile measured by RBS. The index at 1000 cm^{-1} varied in a monotonic fashion with atom fraction of nitrogen x_N, from 3.6 for pure silicon to 3.3 at x_N=0.18 to 2.1 at x_N=0.52.

A rugate-like structure was fabricated by ion implantation at three energies, chosen so that the peaks in the Gaussian-like distribution around the most probable stopping distances (R_p, the projected range) provided the varying composition profile [11]. This filter had a peak reflection of 88%. Ion implantation was found to be impractical as a fabrication method for rugate filters for the following reasons: 1) the maximum thickness was limited by the projected range R_p in silicon of the maximum energy of the nitrogen ion accelerator, 2) the width of the statistical distribution about R_p increases with increasing energy, which prevents precise control of the profile, and 3) available beam currents were too low for a production process. High-current, low-energy ion sources make possible thick rugate film fabrication by simultaneous beam and evaporant deposition.

Homogeneous Films

The amorphous silicon-nitrogen alloy system has been found to have a composition dependence of the index of refraction at 6000 cm-1 [12,13]. Figure 2 shows index vs. composition data for amorphous films as-deposited on silicon substrates that remained <100 C in temperature during deposition. The index, as a bulk property, should not depend on beam energy, so samples from three beam energies are included. The line is a calculation using the Lorentz-Lorenz equation, under the assumption that

$$P_{Si_{(1-x)}N_x} = P_{Si} - x * (P_{Si} - P_{Si_3N_4})/(4/7) \qquad (2)$$

where property P_A denotes the density or the polarization of material A.

The ratio of nitrogen to silicon as measured by RBS of deposited films as a function of the ratio R_{in} of the Faraday cup current density (charges/cm^2/sec) to silicon deposition rate (atoms/cm^2/sec) is illustrated in Fig. 3. The curve in Figure 3 extrapolates to .008 atom fraction of nitrogen at zero beam current, which implies that nitrogen incorporation from the ambient is insignificant at least at low current at the operating pressure. The slope is approximately three, a result of several factors. These include: 1) predominance of molecular ions relative to atomic ions [14]; 2) charge exchange neutralization of a significant fraction of the beam [14]; 3) backscattering of ions from the surface; and 4) sputtering of silicon from the surface, which also causes the curve to be non-linear. Although understanding of the overall shape of the curve is straightforward, interpretation of the specific values and reasons for scatter is the subject of other publications [12,13,15].

The incremental film thickness for a particular R_{in} should be related to

the incremental silicon deposit, if the sputtering, alloy composition, and alloy density are taken into proper account. Homogeneous film thicknesses were determined from surface profilometry, RBS, and fits to infrared spectra. The RBS determination is at present inconsistent with the other methods. Experiments are planned to determine whether assumptions about the density of the films and energy loss of the analyzing beam in the films are in error. Some scatter in the data is also believed to be caused by shifts in the non-water cooled beam-extraction grids during deposition. For historical reasons, the RBS determinations were used as input to the rugate filter fabrication program.

High film purity has been achieved using our nitrogen IBAD of silicon process. For the films with $x_N > 0.08$, oxygen and carbon content in the film bulk is less than the x-ray photoelectron spectroscopy detection limit of 0.01, and hydrogen content is less than 0.01 as measured by elastic recoil detection. In a chamber with higher base pressure, a "silicon" film deposited simultaneously with an IBAD film but shielded from the nitrogen beam contained twenty atomic percent oxygen and little nitrogen. Thus, the ion beam injects nitrogen into the substrate and either removes adsorbed oxygen, or produces a dense deposit which prevents oxygen incorporation upon removal from the chamber.

Experiments are in progress to test film hardness, resistance to chemical attack, wear properties, and adhesion prior to and following high temperature anneals. Results will be reported in future publications. Preliminary findings for slightly nitrogen deficient Si_3N_4 include the following. Knoop hardness (10 gram load) is greater than three times hardness of silicon; films adhere despite >1200 C anneal (Scotch tape test,

ultrasonic cleaning); etching by mixtures of hydrofluoric and nitric acids is much slower than for CVD silicon nitride. Studies of nucleation and growth of the crystalline phases are also underway.

Filter Fabrication

Fabrication of a rugate filter requires good control of the index vs. thickness through the experimentally accessible parameters. Information flow to and from the control computer is illustrated in Figure 1. The model curves of Figures 2 and 3 were used to convert from the current-to-deposition-rate ratio to refractive index, and RBS determinations to convert from the ratio and incremental silicon thickness to alloy thickness. The beam current was normally changed about once per 1.5 nm of deposited silicon, with other variables such as beam voltage, evaporation rate set point and chamber pressure held constant.

A number of rugate filters have been fabricated with peak reflections in the 1 to 3 micrometer range. A twenty-three cycle $Si_{(1-x)}N_x$ rugate whose deposition record is found in Figure 4 represents the largest number of cycles that we have produced at these wavelengths. The ratio of the total Faraday cup current in microamps to the quartz monitor indicated silicon deposition rate in Angstroms/sec, is plotted versus the integrated silicon deposition. The abscissa is related to R_{in} through the electronic charge, the density of silicon and the Faraday cup aperture area, 0.14 cm^2. During the deposition, the quartz monitor was subject to large instantaneous fluctuations in indicated rate, which account for the sharp features of the deposition record. After a thermal anneal for 30 minutes at 750 C, the transmission spectrum was taken, and is plotted in Figure 5 as (-

log(transmission)) vs wavelength (micrometers). The optical density at λ=1.15 micrometers is 2.6, with $\Delta\lambda/\lambda$=.08 (full width, half maximum of optical density). The long wavelength range is similar to the interference pattern that would be obtained with a homogeneous film of the same average index on silicon. The short wavelength region is dominated by absorption in the underlying silicon substrate. The fabrication method is clearly successful.

A theoretical transmission spectrum was calculated from the actual deposition record and the data of figures 2 and 3 and is included for illustrative purposes. Since the RBS determinations of alloy thickness have been found inconsistent with other thickness determinations, a constant factor was used to convert from the quartz monitor thickness of the deposition record to the alloy thickness. The peak position is sensitive only to the product of the cycle thickness and the average refractive index. In the calculation, absorption was not taken into account, so the calculated curve of Figure 5 deviates from the measured spectrum at short wavelengths. The calculated peak optical density is only 0.2 larger than the measured value for the sample of Figure 5, which gives confidence that rugate filters with larger numbers of cycles should yield higher optical density.

Summary

In conclusion, nitrogen ion-beam-assisted deposition of silicon has been shown to be a practical method for deposition of rugate filters upon silicon substrates. Quartz monitor control on the deposition with dynamic computer control of the Faraday cup current to produce sinusoidal index variation with depth is adequate to make infrared filters with high optical densities. The filters have excellent mechanical, thermal, and chemical stability, and

adhere to the silicon substrates despite anneals up to 1200 C.

References

1. E.Hecht and A.Zajak, Optics, Addison Wesley, Reading, MA (1979)

2. C. Strecker, W. Johnson, and J. Davison "The Preparation of a SiGe Rugate Variable Index Optical film by a Solid State Diffusion Process" AFWAL-TR-85-4087 (1985)

3. G.K. Hubler, E.P. Donovan, D. Van Vechten, R.H. Bassel and D.R. Brighton, "Ion Beam Assisted Deposition of Optical Coatings" NRL Memorandum Report 5927, 1987.

4. S.M. Rossnagel, and J.J. Cuomo, MRS Bulletin 12 (1987) 40-49

5. E.H. Hirsh and I.K. Varga, " Thin Film Annealing by Ion Bombardment" Thin Solid Films, 69, 99 (1980).

6. D.R. Brighton, and G.K. Hubler "Binary Collision Cascade Prediction of Critical Ion-To-Atom Arrival Ratio in the Production of Thin Films With Reduced Intrinsic Stress" Nucl. Inst. And Meth. B28 (1987) 527

7. See, for example, W.K. Chu, J.M. Mayer, and M. Nicolet, Backscattering Spectroscopy, Academic Press, New York (1978)

8. L.R. Doolittle, "Algorithms for the Rapid Simulation of Rutherford Backscattering Spectra" Nucl. Instr. and Methods B9 (1985) 344

9. O. Heavens, Optical Properties of Thin Solid Films Dover Publications, New York,NY (1965)

10. G.K. Hubler, P.R. Malmberg, and T.P. Smith, III, "Refractive Index Profiles and Range Distributions of Silicon Implanted with High-Energy Nitrogen" J. Appl. Phys. 50 (1979) 7147

11. G.K. Hubler, P.R. Malmberg, and T.P. Smith III, "Ion-Implanted Multilayer Optical Interference Filter" Patent #4,262,056 (1981)

12. E.P. Donovan, D.R. Brighton, G.K. Hubler, and D. Van Vechten, "Ion Beam

Assisted Deposition of Substoichiometric Silicon Nitride" Nucl. Instru. Meth., B19/20 (1987) 983

13. E.P. Donovan, D.R. Brighton, D. Van Vechten and G.K. Hubler, "Infrared and Ion Beam Analysis of Si_xN_{1-x} Alloys Grown by Ion Beam Assisted Deposition" in M. Wittmer, J. Stimmell and M. Strathman, Material Issues in Silicon Integrated Circuit Processing, Materials Research Society, Pittsburgh,PA (1986) 487

14. D. Van Vechten, G.K. Hubler, and E.P. Donovan, "Characterization of a 3 cm Kaufman Ion Source with Nitrogen Feed Gas" Vac. Technol. Appl. & Ion Physics 36 (1986) 841

15. D. Van Vechten, G.K. Hubler, and E.P. Donovan, "Summary Abstract: Factors Important to Achieving Compositional Control and Reproducibility in a Reactive Ion Beam Assisted Deposition Process" J. Vac. Sci. and Tech. (1988)

Fig. 1. Schematic diagram of ion beam assisted deposition (IBAD) system. 1) Electron beam evaporator with silicon charge. 2) Kaufman ion source with nitrogen feed gas. 3) Faraday cups with secondary electron suppression. 4) Quartz crystal evaporation monitor.

Fig. 2. Refractive index at 6000 cm^{-1} vs. nitrogen atom fraction in as-deposited films.

Fig. 3. Film nitrogen to silicon ratio vs. R_{in}, incident charge-to-silicon flux ratio for 500 eV nitrogen beam assisted silicon evaporation.

Fig. 4. Deposition record of 23 cycle rugate filter on silicon.

Fig. 5. ($-\log_{10}$(transmission)) vs. wavelength for rugate filter of Figure 4 after 750 C anneal. Absorption in substrate occurs at low wavelengths.

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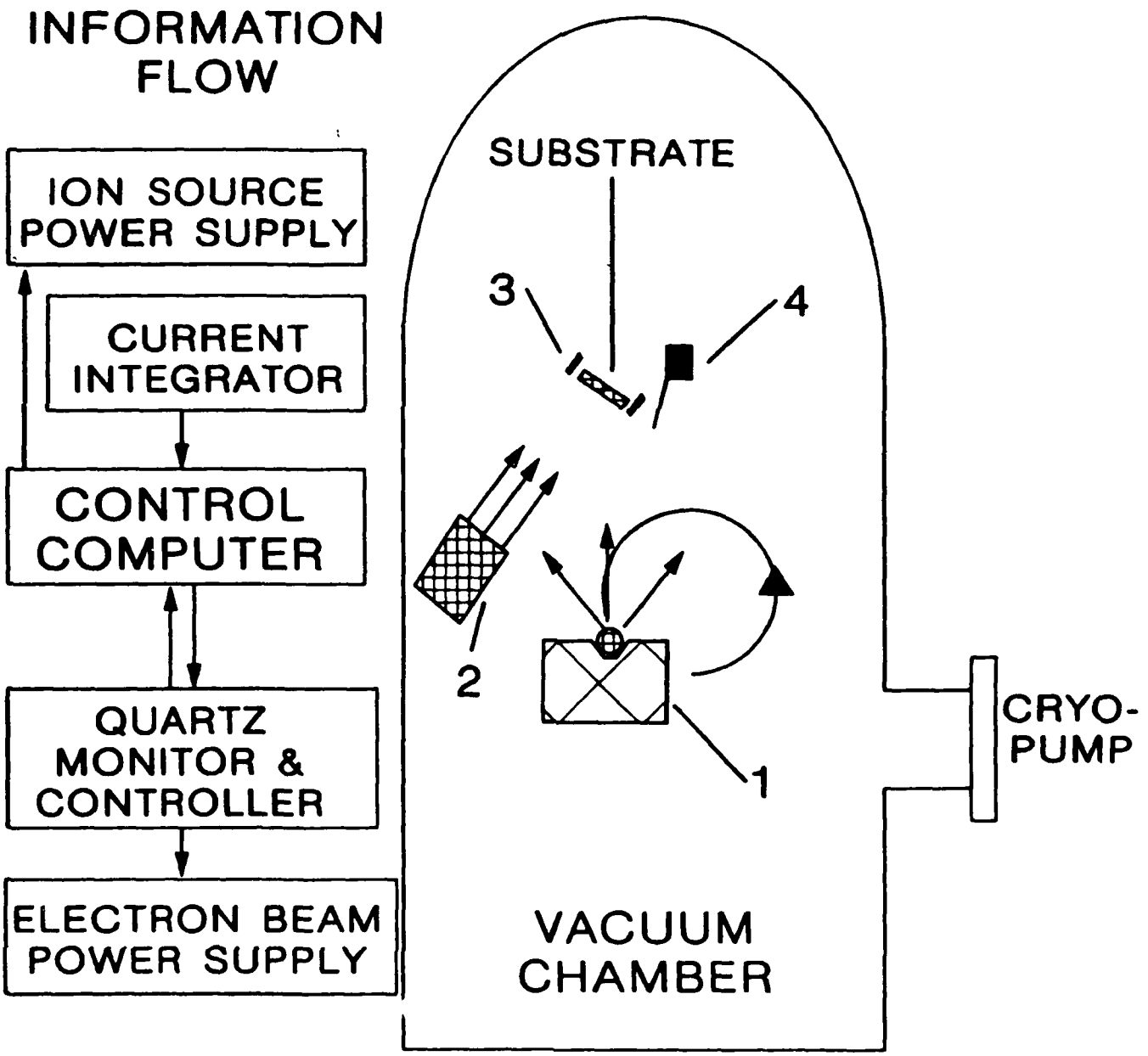

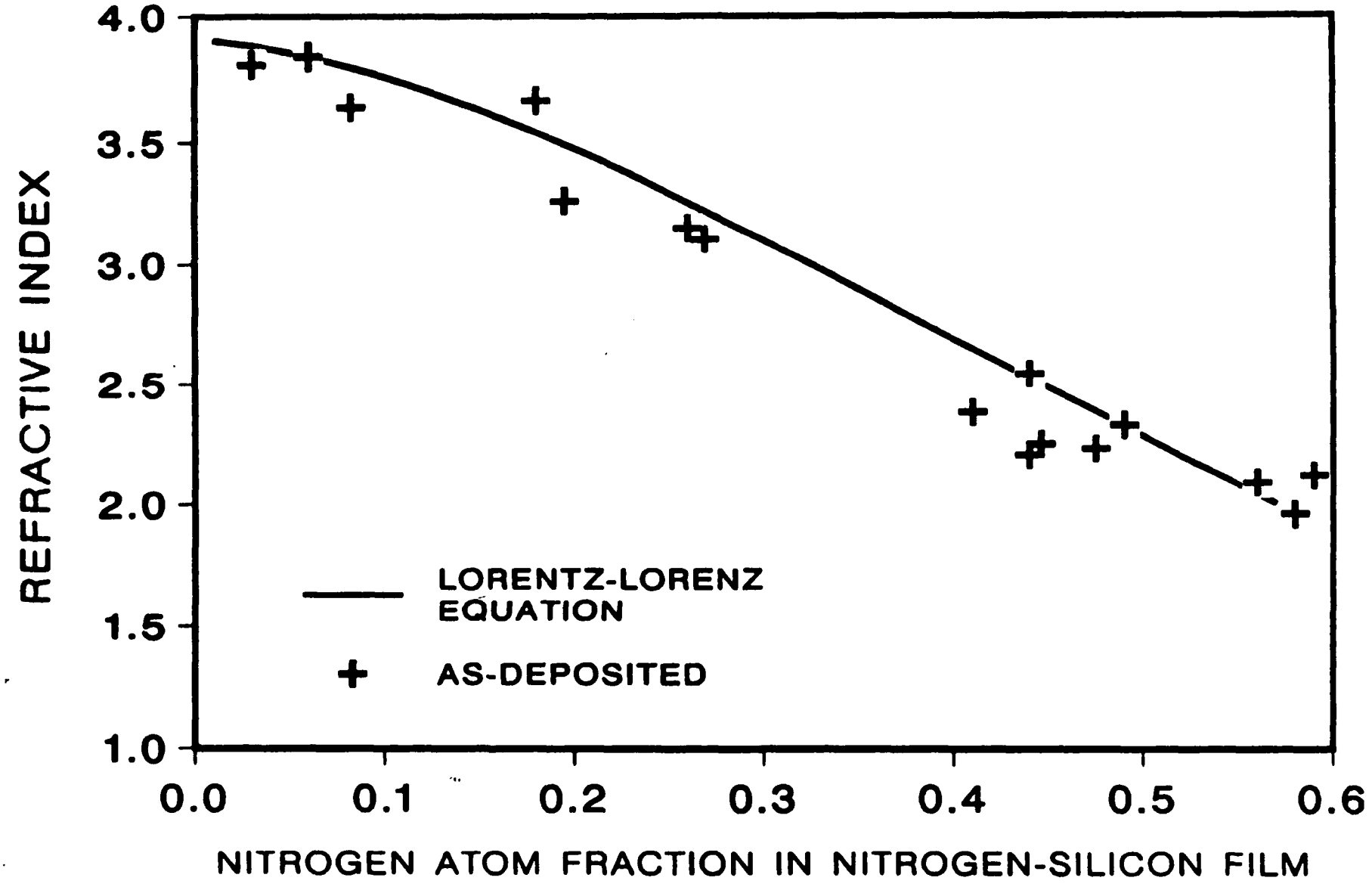
4.0
3.5
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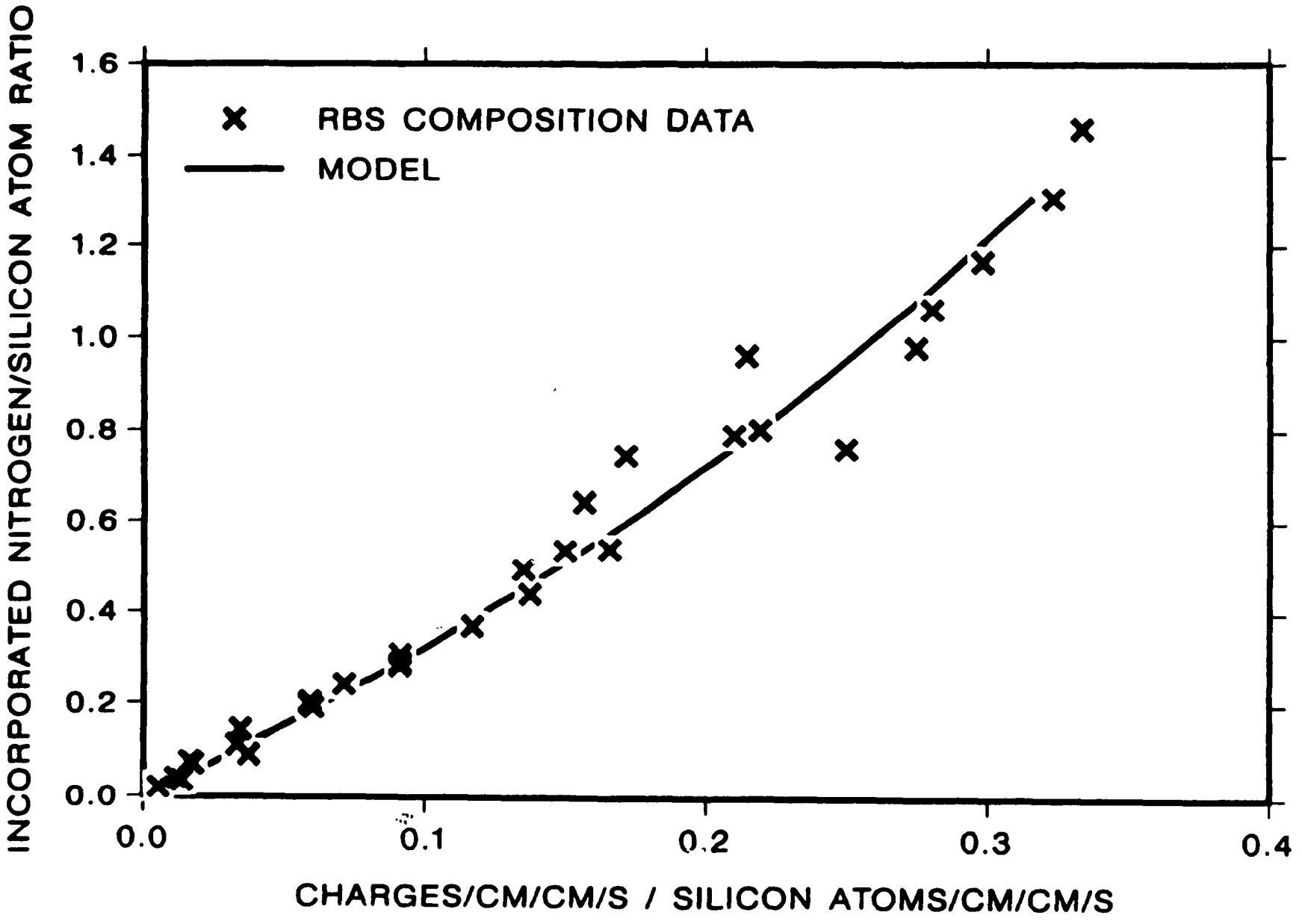
REFRACTIVE INDEX
LORENTZ-LORENZ EQUATION
AS-DEPOSITED
0.0
0.1
0.2
0.3
0.4
0.5
0.6
NITROGEN ATOM FRACTION IN NITROGEN-SILICON FILM

flux ratio for 500 eV nitrogen beam assisted silicon evaporation.



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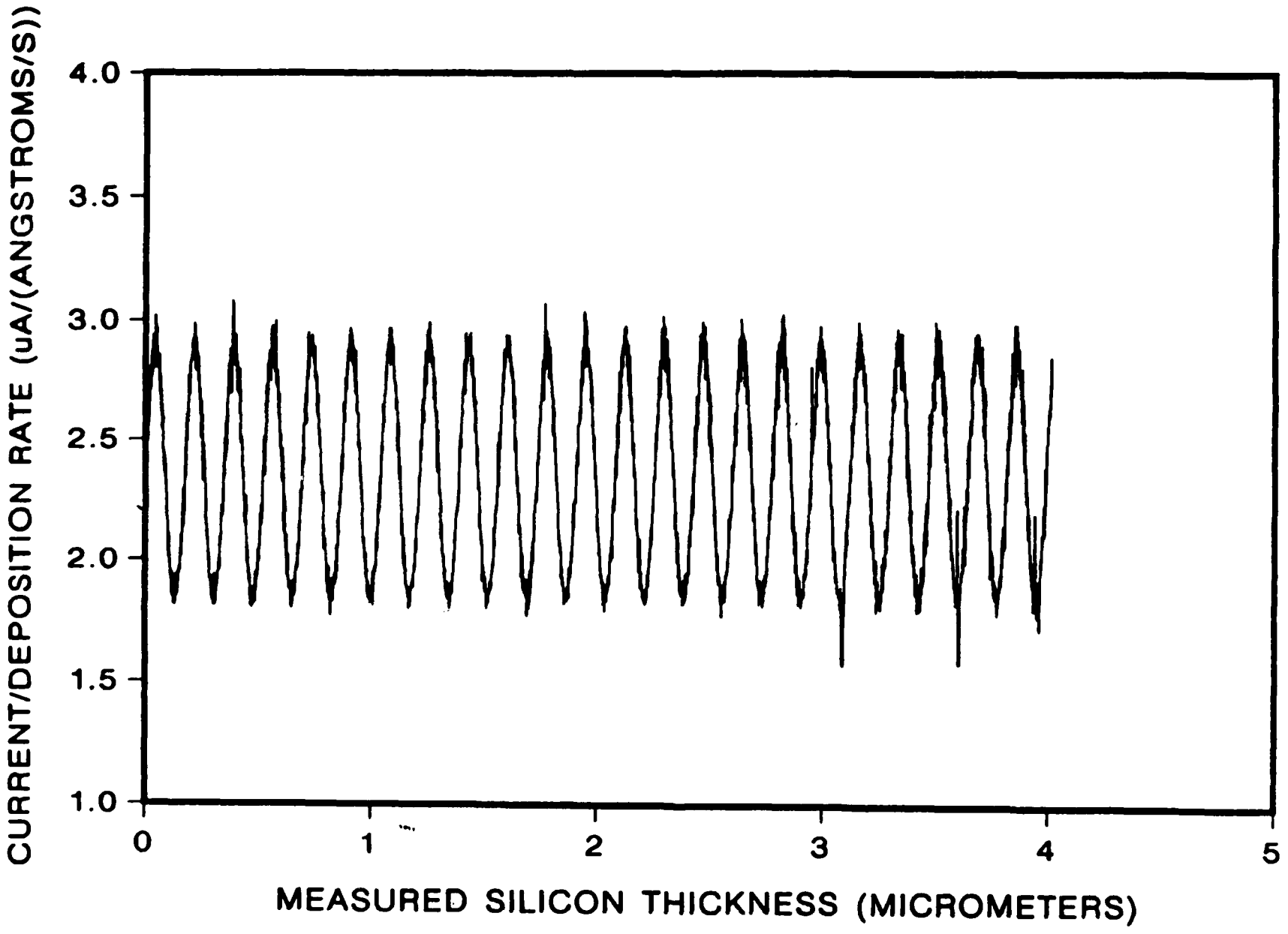

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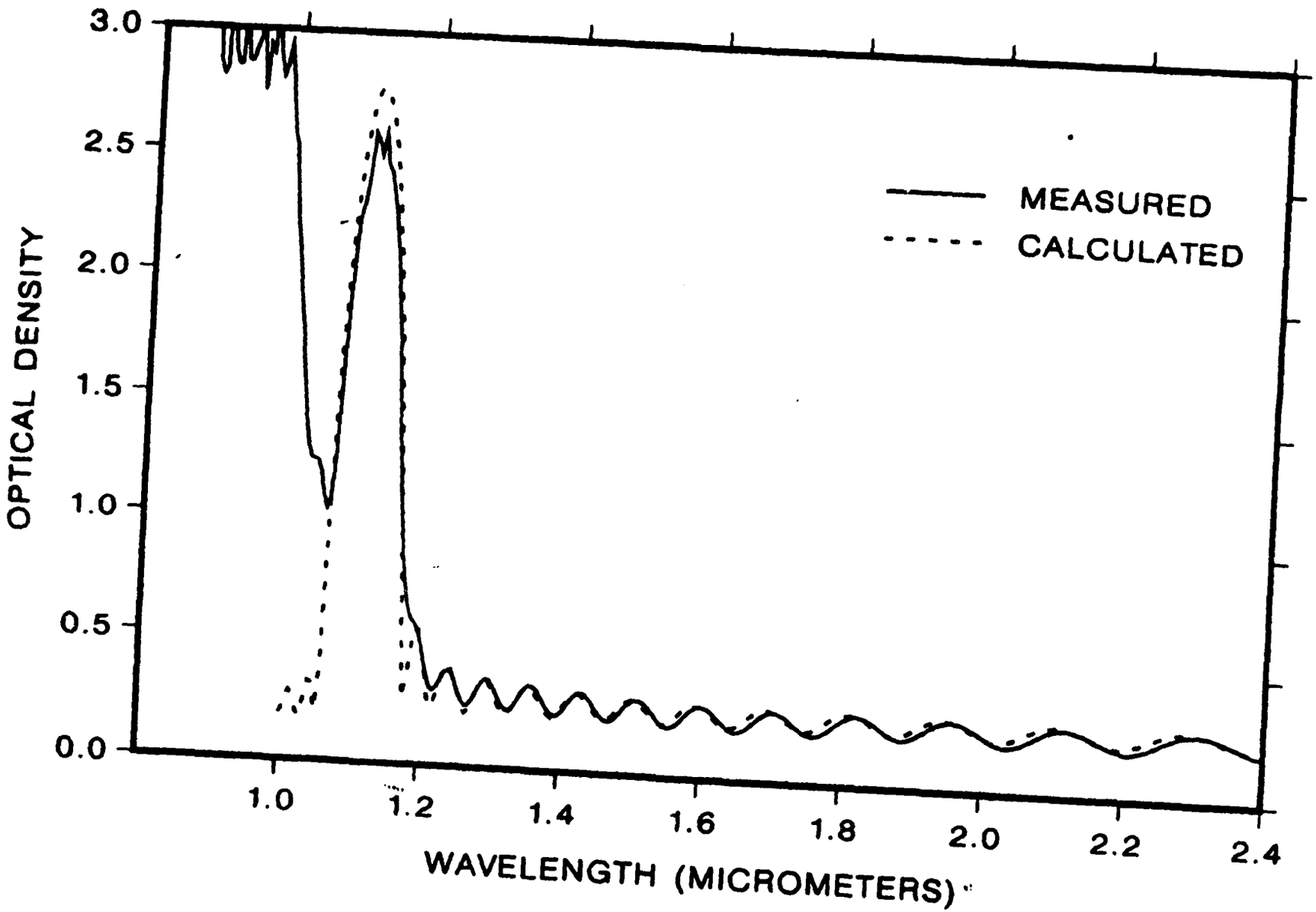

THERMAL STABILITY OF SILICON NITRIDE COATINGS PRODUCED BY ION ASSISTED DEPOSITION

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Amorphous Si-N alloy films containing from about 20 to 60 at. % N were deposited by combined e-beam evaporation of Si and ion bombardment of N. A Kaufman-type ion gun produced the 500-eV nitrogen ion beam. Films up to 1-μm thick were deposited on single-crystals of silicon and sapphire in a vacuum of about 2×10^{-4} torr. The as-deposited films were characterized by Rutherford backscattering spectroscopy for composition, visible and near-infrared spectrophotometry to measure index of refraction and absorption bands from Si-N bond vibrations, and X-ray diffraction for crystal structure. Subsequently, samples were annealed in a thermogravimetric analyzer at temperatures up to 1350°C to ascertain their thermal stability against crystallization, oxidation, and reaction with the substrate. Postanneal examination by Rutherford backscattering, spectrophotometry, X-ray diffraction, and optical and scanning electron microscopy provided detailed information on the thermally induced changes in the films. Crystallization of Si occurred in N-poor samples, while αSi_3N_4 crystallized in N-rich samples after 1200°C anneals. Blisters sometimes also appeared following 1200°C anneals of N-rich samples. For anneals up to 1200°C, no reactions with sapphire or Si substrates were observed and minimal oxidation was found.

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1. INTRODUCTION

Previously Donovan et al. [1-3] have developed the ion assisted deposition (IAD) technique for making Si-N alloy films of uniform composition up to 1 μm thick. They were able to continuously vary the N content in the films from 0 to 63 at. % N. Such films were found to be amorphous, dense, corrosion resistant, and adherent to single crystal Si substrates. Evidence of film structural relaxation was found after a 2h anneal at 900°C for films containing up to about 20 at. % N [1,3].

This work addresses the thermal stability of IAD films containing up to about 60 at. % N, and for annealing temperatures up to 1350°C. Single crystal substrates of both Si and sapphire were used to evaluate possible film/substrate interactions at these higher temperatures. Film composition, microstructure, and optical properties were examined.

2. EXPERIMENTAL PROCEDURE

Si substrates were cut from p type, B doped <111> and <100> Si wafers. Sapphire substrates with c <00.1>, m <10.0>, and a <11.0> plane orientations were used in the as-received condition. Substrates were cleaned with acetone after mounting with silver print, and sputter cleaned with the ion beam just prior to film deposition.

Details of the film deposition equipment and procedures have been previously described by Van Vechten et al. [4,5] and Donovan et al. [1,2]. For this work a Si evaporation rate of 0.5 nm/s was used. The N flux was

altered by changing the cathode current of a Kaufman ion source operated at 500 eV. From previous work [5] the ion beam was expected to consist of 89% diatomic and 11% monatomic ions, plus some neutralized N. The substrates were aimed at the ion gun. Atom arrival rate ratios of N/Si between 0.17 and 0.8 were used to produce uniform films typically 300 to 500-nm thick containing between 17 and 60 at. % N. The substrates were maintained in a vacuum of about 2×10^{-4} torr during film deposition.

Film composition was determined by 2.0 MeV $^4He^{++}$ Rutherford backscattering spectroscopy (RBS) using the RUMP computer program [6]. Crystalline structure was determined by θ-2θ X-ray diffraction (XRD) using Cu K_α X-rays, a curved graphite monochromator, and a 0.125 deg/min scan rate. The index of refraction was evaluated as a measure of film structural relaxation using a technique described by Hubler et al. [7]. The Restrahlen absorption bands below 1000 cm^{-1} showing information about Si-N bonds [8,9] were examined using Fourier transform infrared spectrometry (FTIR). Optical and scanning electron microscopy (SEM) were performed as necessary.

Samples were annealed in a thermogravimetric analyzer under high purity Ar flowing at 60 cm^3/min. After insertion into the cool furnace the temperature was increased at a rate of 40°C/min up to the annealing temperature. Samples were cooled in the furnace at a rate of about 40°C min, down to about 800°C before exposure to the atmosphere.

3. RESULTS AND DISCUSSION

Films with a N content below 20 at. % had previously exhibited structural relaxation of Si upon annealing to 900°C for 2h [1]. This was observed by a change in the index of refraction of the deposited film. However, X-ray diffraction in this work of a sample containing 18 at. % N after annealing at 900°C for 2h followed by 950°C for 0.5h revealed no additional diffraction peaks beyond the substrate Si (111) peak.

Films containing about 20 to 30 at. % N and deposited on Si exhibited Si crystallization upon annealing at 1200°C for 45 minutes. Under these conditions, randomly oriented polycrystalline Si formed as determined by XRD. The volume fraction of crystalline Si diminished as the N content increased. However, a nominally 30 at. % N film on a-plane sapphire and annealed at 1200°C for 45 min showed no evidence of Si crystallization, but did show small spherulites of αSi_3N_4 by optical microscopy.

The low temperature phase αSi_3N_4 crystallized in films on Si containing more than about 30 at. % N but less than the stoichiometric amount (57.1 at. %) when annealed to temperatures in excess of about 1100°C. The morphology of the precipitates is particularly interesting, as shown in Fig. 1. While such spherulites were previously observed in Si-N alloys formed by ion implantation [10] , these are considerably more well formed. These spherulites would normally be difficult to see in the optical microscope, since crystallization only slightly changes the index of refraction of Si_3N_4 [11,12]. However, αSi_3N_4 has an hexagonal structure and is therefore birefringent. Since the precipitates usually formed with the c axis inclined to the sample normal, the spherulites could be viewed with crossed polarizers in the optical microscope. In fact, the c axis was

frequently found to lie in the plane of the sample surface as shown in Fig. 2 for a sample annealed at 1200°C for 3 min followed by 1250° for 1h. The predominant peaks found by symmetric XRD are all of the hk0 variety. This occured for both Si <100> and <111> orientations. Further annealing disrupted this preferred orientation. A more detailed discussion of the precipitate morphology and growth kinetics of the spherulites will be presented elsewhere.

Another feature found after annealing films containing more than about 30 at. % N was blisters, as shown in Fig. 3. These were found on films deposited on both sapphire and Si substrates, although they appeared to occur more readily on sapphire substrates. The blisters formed after annealing in excess of 1100°C and are believed to occur due to agglomeration of N in the film into bubbles containing N_2 gas, or as a result of film delamination from the substrate due to stress. The blisters are not believed to form during specimen cooling since the spherulite number density is frequently diminished in the immediate vicinity of the blisters.

For films containing a nearly stoichiometric amount of N (57.1 at. %), no evidence of αSi_3N_4 crystallization was found for films on sapphire substrates by optical microscopy after annealing up to 1200°C for 1h. Crystallization did occur on Si substrates, usually after a 1200°C anneal, but in one case required an anneal up to 1350°C for 1h. Perhaps excess Si aids the nucleation process.

Very little oxidation or interaction with either the Si or sapphire substrates was observed by RBS for films containing more than 40 at. % N

4. CONCLUSIONS

Amorphous IAD alloy films of Si and N were readily made up to the stoichiometric composition of αSi_3N_4. For N content between 30 and 50 at. %, these films remained amorphous and stable up to about 1100°C for 1h. Transformations occured by Si or αSi_3N_4 crystallization, and by blister formation. Nominally stoichiometric films on sapphire and in one case on Si were more resistant to crystallization, but more prone to blister formation. Little oxidation or interaction with substrate Si or sapphire was found for anneals up to 1200°C.

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REFERENCES

[1] E.P. Donovan, D.R. Brighton, G.K. Hubler, and D. Van Vechten, Nucl. Instr. and Meth. B19/20 (1987) 983.

[2] E.P. Donovan, D. Van Vechten, A.D.F. Kahn, C.A. Carosella, and G.K. Hubler, submitted to Applied Optics.

[3] E.P. Donovan, D.R. Brighton, D. Van Vechten, and G.K. Hubler, Mater. Res. Soc. Symp. Proc. 71 (1986) 487.

[4] D. Van Vechten, G.K. Hubler, and E.P. Donovan, to be published in J. Vac. Sci. Technol. A.

[5] D. Van Vechten, G.K. Hubler, and E.P. Donovan, Vacuum 36 (1986) 841.

[6] L.R. Doolittle, Nucl. Instr. and Meth. B9 (1983) 344.

[7] G.K. Hubler, P.R. Malmberg, and T.P. Smith III, J. Appl. Phys. 50 (1979) 7147.

[8] J.A. Borders and W. Beezhold in Ion Implantation in Semiconductors, eds., I. Ruge and J. Graul (Springer, New York, 1971) p. 241.

[9] Yu. N. Volgin and Yu. I. Ukhanov, Opt. Spectrosc. 38 (1975) 412).

[10] J. Belz, E.H. Te Kaat, G. Zimmer, and H. Vogt, Nucl. Instr. and Meth. B19/20 (1987) 279.

[11] E.A. Taft, J. Electrochem. Soc. (1971) 1341.

[12] John T. Milek, Silicon Nitride for Microelectronic Applications, Part 1. Preparation and Properties, in series, Handbook of Electronic Materials, Vol. 3 (IFI-Plenum, New York, 1971) p. 54.

FIGURES CAPTIONS

Fig. 1. Optical micrograph of spherulites formed in nominally 30 at. % N film deposited on Si <100> after annealing at 1200°C for 45 min. Crossed polarizers were used to view otherwise invisible optically active precipitate.

Fig. 2. X-ray diffraction scan for sample with more fully developed spherulites. Reference bars are from powder data file for αSi_3N_4. Note the strong prevalence of hk 0-type reflections. This sample had 54 at. % N, was on Si <100> and was annealed for 3 min at 1200°C, followed by 1h at 1250°C.

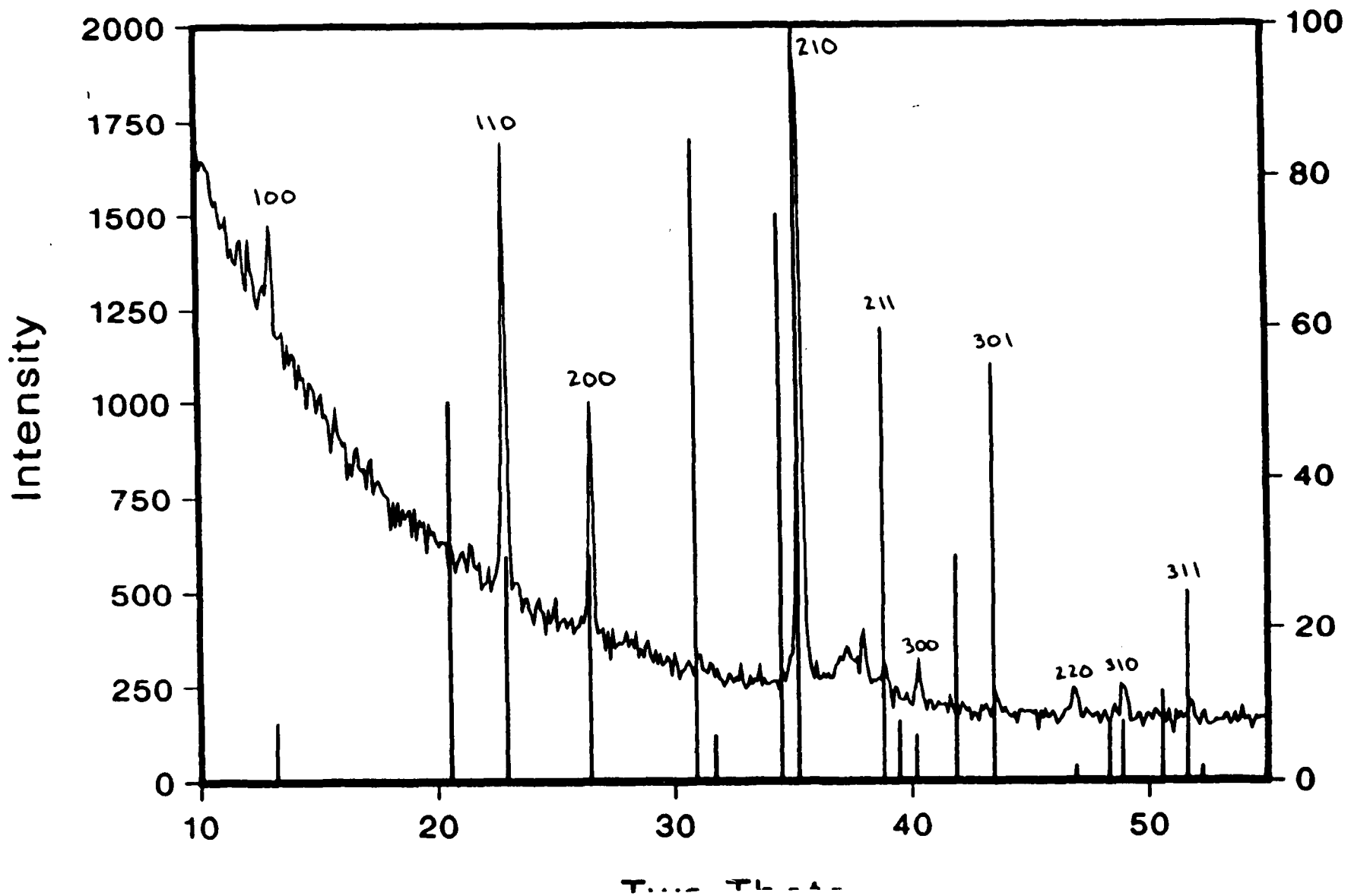
Fig. 3. SEM photo showing blisters formed on nominally stoichiometric Si_3N_4 film deposited on a-plane sapphire and annealed for 15 min at 1150°C. No spherulites were observed by optical microscopy.

Fig. 4. Optical micrograph series showing evolution of blisters upon annealing of stoichiometric film on Si <100> for 1h at a) 1250°C, b) 1300°C, and c) 1350°C. The blisters rupture, allowing oxidation of underlying Si.

Fig. 5. FTIR transmission scans with substrate Si absorption removed showing Restrahlen absorption from Si-N bond vibrations in 49 at. % N film on Si <100>. Broad peak is from amorphous as-deposited sample, sharper peak with more structure is from sample after isochronal anneals ending at 1250°C where substantial αSi_3N_4 crystallization was observed.

Fig. 6. FTIR transmission scans of 49 at. % N film after 1100°C-1h anneal where little relaxation of amorphous structure was seen, and also of sample shown in Fig. 4c after oxide was etched away by HF acid. Onset of Si_3N_4 crystallization can be seen.

10kV 8 21kX WD 22 8U 555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1500
1250
1000
750
500
250
0
100
80
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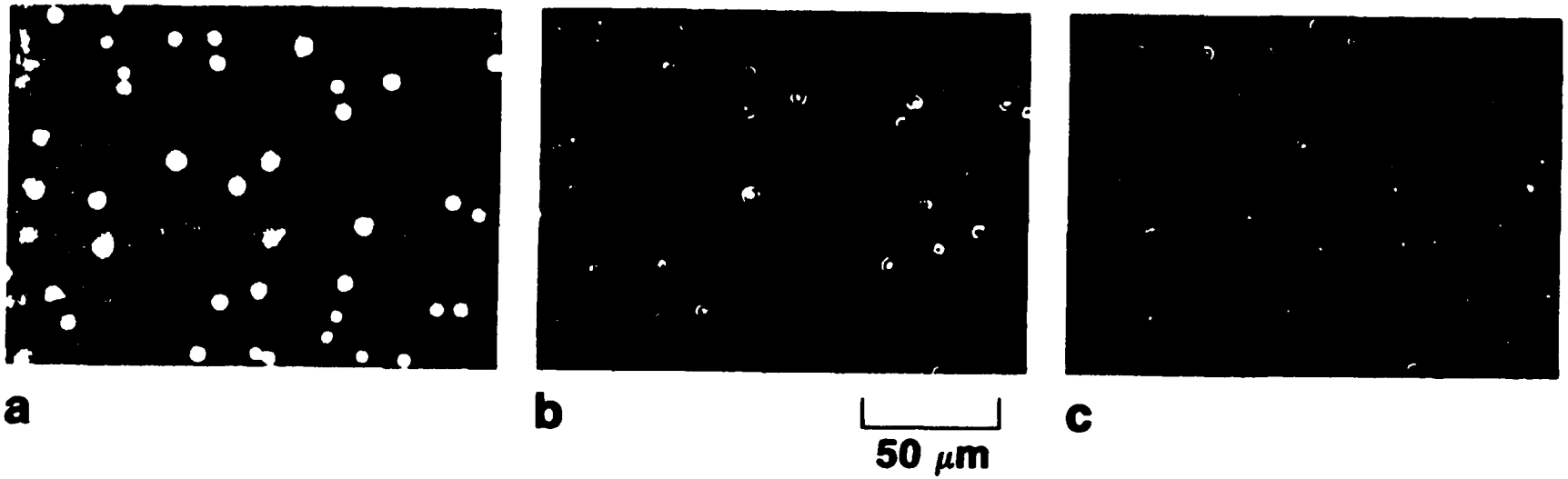
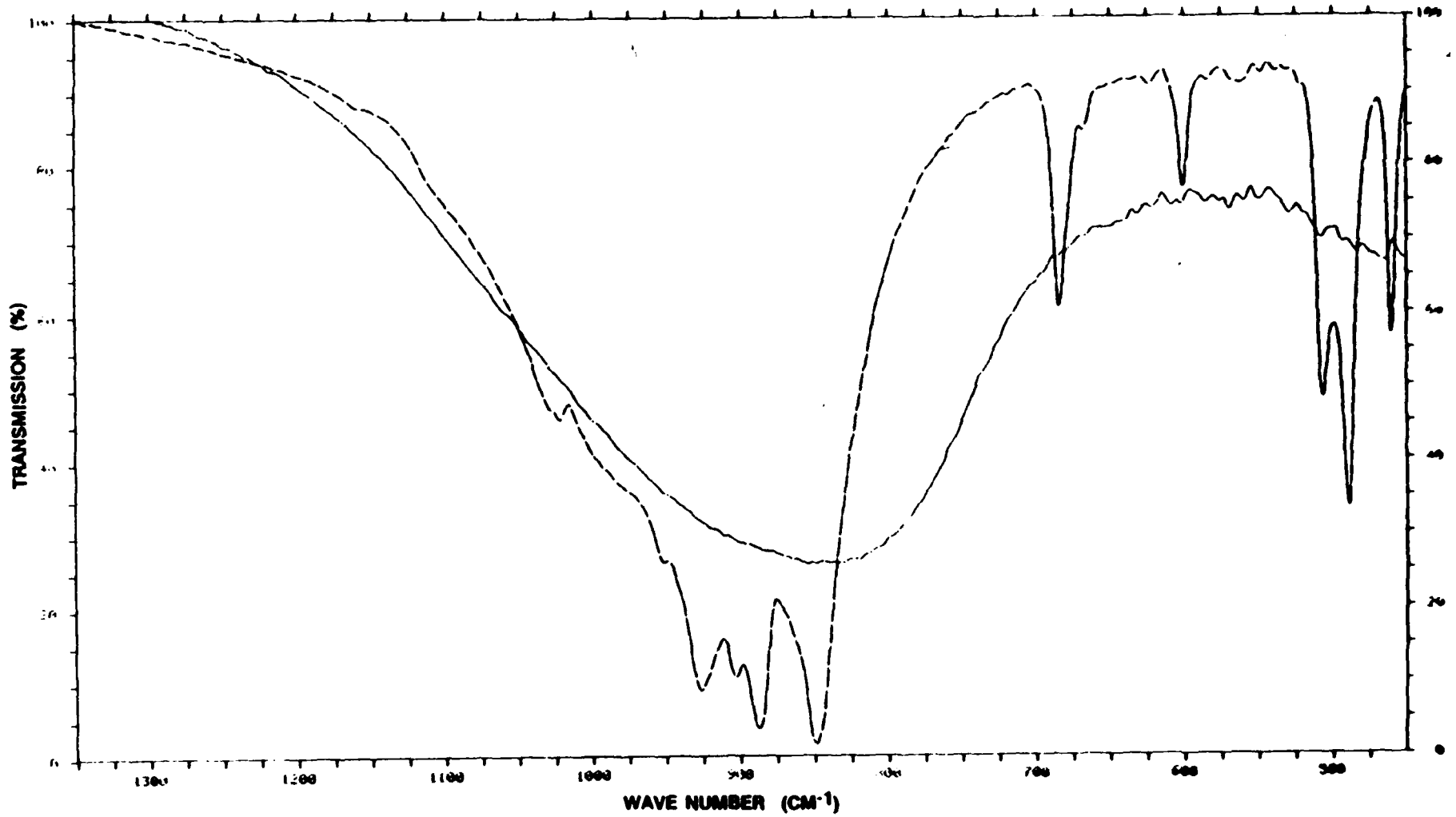
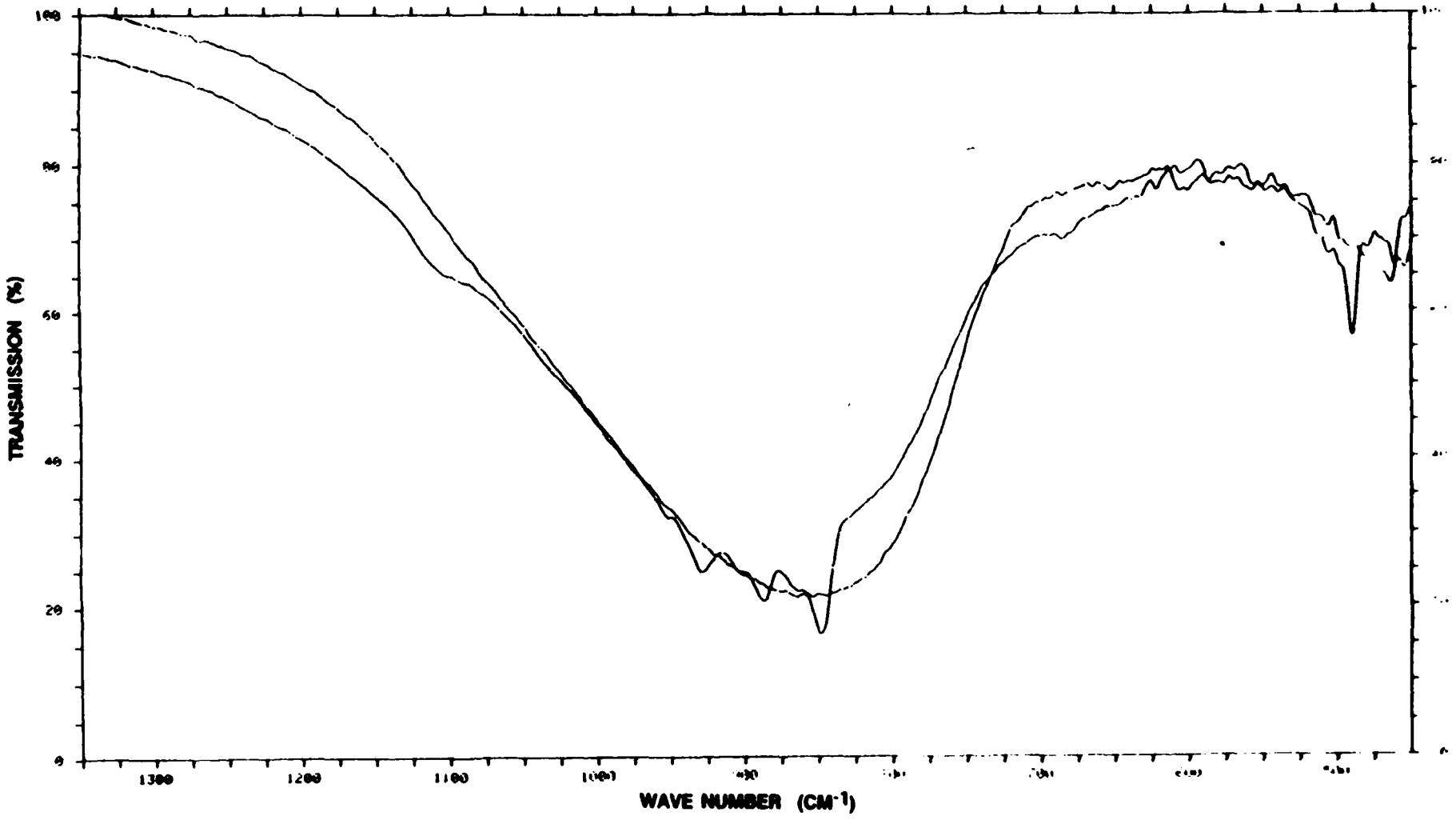
50
100
110
200
210
211
300
301
220
310
311

2 Pg


a
b
50 μm
c

100 μm


TRANSMISSION (%)
WAVE NUMBER (CM-1)


TRANSMISSION (%)
100
80
60
40
20
0
1300
1200
1100
WAVE NUMBER (CM-1)